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14. ABSTRACT
This program enabled a comparison of the electromechanical measurements on high strain piezoelectric single crystal materials between groups at Alfred University, TRS Ceramics, the Royal Military College of Canada, the Naval Undersea Warfare Center, and Penn State University. This work focused on the measurement of field-induced polarization and strain in single crystal PZN-PT and PMN-PT under nominally stress free conditions. The objective of this work was to assess the effect of measurement technique on the observed behavior of these two single crystals. The research enabled a test of the applicability of a protocol for the derivation of small and large signal dielectric constants from the polarization versus field curves and the small and large signal piezoelectric coefficients from the strain versus field curves. Two PZN-PT compositions (4.5% PT and 8% PT), and two PMN-PT compositions (30% PT and 25-28% PT) were characterized. It was found that the different groups showed generally very good agreement in the measured properties.

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15. SUBJECT TERMS

Contract Information

Contract Number	N00014-00-1-0826
Title of Research	The Effect of Technique on the Measurement of the Electromechanical Material Properties in Piezoelectric Single Crystals
Principal Investigator	Susan Trolier-McKinstry, Wes Hackenberger, and Lynn Ewart
Organization	Penn State University, TRS Ceramics, and NUWC

Technical Section

Technical Objectives

Piezoelectric single crystals, such as PMN-PT and PZN-PT, are under development as active naval sonar transducer materials. The high coupling coefficients exhibited by these materials makes them strong candidates for broadband applications. Numerous programs are underway, sponsored by DARPA and ONR, to optimize the fabrication of these single crystals and to develop appropriate prototype transducer designs for several applications.

Accurate characterization of the properties of PMN-PT and PZN-PT single crystals is necessary to support both the materials research community and transducer designers. Of particular interest is the field dependent polarization and strain response from which the low signal and effective large signal dielectric constant and the electromechanical coefficients (piezoelectric and electrostrictive) can be derived. Producing accurate data requires correct measurement technique and data analysis. Yet, standardized measurement setups, procedures and data analysis techniques for deriving properties have not been established in this area.

Recent experiences in the scientific community indicate that the measurement of the field dependent polarization and strain response may be more problematic than the same measurements in polycrystalline electroactive ceramics. Several concerns are evident. First is the fact that the strain levels can be a factor of ten higher than piezoelectric ceramics like PZT. In addition, the strain – field curves of the relaxor-based materials can be quite non-linear, particularly when domain reorientation is contributing to the measured response. In addition, the relaxor-based materials appear to be appreciably more stress sensitive, even at very low loads, than materials like PZT. For example, the coupling constant of parallel wired stacks of single crystal PMN-PT dropped from 0.93 to 0.83 when stiff electrodes were used instead of more compliant electrodes. Small changes in the pressure applied by specimen holders caused dramatic differences in the observed strain versus electric field behavior of a PZN-8%PT crystals. Coupled with these experimental concerns is the fact that an accepted procedure does not currently exist for deriving the small and large signal dielectric constants from the polarization versus field curves and deriving the small and large signal electromechanical coefficients from the strain versus field curves.

This work focused on the measurement of field-induced polarization and strain in single crystal PZN-PT and PMN-PT under nominally stress free conditions. The objective of this work was to assess the effect of measurement technique on the observed behavior of these two single crystals. The research enabled a test of the applicability of a protocol for the derivation of small and large signal dielectric constants from the polarization versus field curves and the small and large signal piezoelectric coefficients from the strain versus field curves. Two PZN-PT compositions (4.5% PT and 8% PT), and two PMN-PT compositions (30% PT and 25-28% PT) were characterized.

Technical Approach

Differences in measurement technique arise from variations in experimental setup and operators. To introduce both these variables into this research, five different research groups participated in testing. The persons responsible for the data collection and analysis are given in parentheses after the institution.

1) The UTMR at NAVSEA, Newport (Lynn Ewart, Hal Robinson)
2) Penn State (Susan Trolier-McKinstry)
3) TRS Ceramics (Paul Rehrig, Wes Hackenberger, Ed Alberta)
4) Royal Military College (Binu Mukherjee, Shi-Fang Liu, Wei Ren)
5) Alfred University (Steve Pilgrim)

A synopsis of the measurement equipment employed by each group is given in Figure 1.

Single crystals with compositions on the rhombohedral side of the morphotropic phase boundary (MPB) have the best electromechanical properties. Thus, it is important to include near - MPB compositions in the current study. However, there is also strong incentive to explore compositions away from the MPB in order to avoid the problem of driving the materials across the phase boundary during electrical excitation. The latter can lead to increased levels of hysteresis in the measured data, as well as instability in the dielectric and electromechanical properties. To ensure the crystals are significantly far from the MPB, PMN with 25-28% PT and PZN with 4.5% PT were also studied. Electroded and poled single crystals for this study of all compositions except (PMN-30%PT) were supplied by TRS Ceramics.

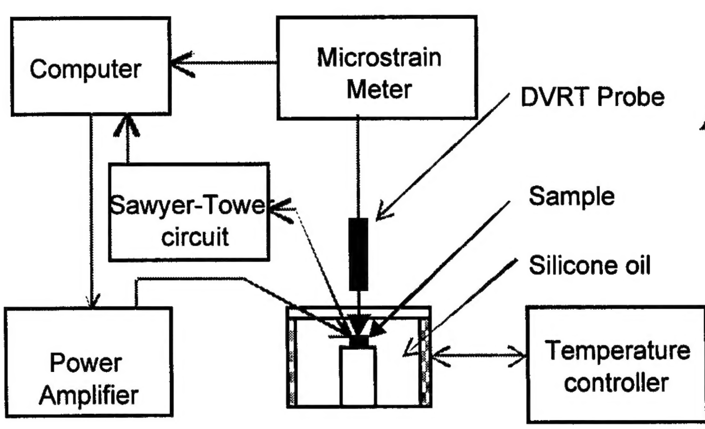
Figure 1: Facilities used in crystal characterization

RMC:

microstrain DVRT (differential variable reluctance transducer) probe

"small" force on top electrode

1 Hz, room temperature



RMC measurement equipment

NUWC:

LVDT probe

1or 2 Hz, room temperature

PSU/TRS:

Schaevitz LVDT probe

"low" force top contact

1 Hz, room temperature

Alfred:

Fotonic™ sensor

1 Hz, room temperature

"low" force top contact

Results

A protocol was established for measuring the properties of single crystal piezoelectrics. It is available at http://utmr.npt.nuwc.navy.mil. Three sets of measurements were made by each group:

1) Measurements to validate the piezoelectric single crystal protocol:
   - Measure strain and polarization responses at a bias electric field, $E_{bias} = 0.635$ MV/m with a 0.635 MV/m swing. From these data, ε_{33}(s,MIE = 0.635 MV/m) and d_{33}(s,MIE=0.635 MV/m) were calculated from the instantaneous slope of average curves at 0.635 MV/m
   - Measure strain and polarization responses at $E_{bias} = 0.67$ MV/m with 0.34 MV/m oscillation. ε_{33}(l,Ml) and d_{33}(l,Ml) were calculated as linear approximations to the endpoints of the data
   - Calculate large signal tan δ

2) Unipolar strain and polarization measurements to 1.0, 2.0 and 3.5 MV/m

3) Bipolar strain and polarization measurements to 1.0, 2.0 and 3.5 MV/m, and calculate the remanent polarization, P_r, and the coercive field, E_c.

Tables 1 – 4 show the results of the protocol measurements for PZN-4.5%PT, PZN-8%PT, PMN-26±1% PT and and PMN-29±1%PT. It can be seen there that the agreement between the groups is reasonable for all of the compositions. In all cases, there was some curvature associated with the strain and polarization response as a function of electric field, which leads to the high field properties being somewhat smaller then the small signal values.

At higher electric field drive levels, the onset of hysteresis was observed in the unipolar measurements of strain and polarization. It was found that the PZN-4.5%PT samples did not show much hysteresis for drive levels up to 2MV/m. A small amount of hysteresis associated with the field induced rhombohedral – tetragonal phase transformation was observed at drive levels of 3.5 MV/m (See Figure 2). In contrast, the PZN-8%PT samples were considerably more variable in the field level required for the onset of the field – induced phase transformation. As a result, the properties were considerably more variable, and the large signal dielectric loss was considerably higher. Cryogenic poling of the PZN-8%PT reduced the sample- to -sample variability somewhat, although the samples were still fairly lossy. PMN-26 ±1% PT and PMN-29±1% PT samples showed somewhat lower piezoelectric coefficients (as expected), but no indication of field- forced phase transformations over the measurement range utilized. NUWC calculated the effective dielectric and piezoelectric coefficients for the large field excursions measured by each group (See Tables 5 – 8). As a note, many of the data for Alfred University are missing because numerous crystals underwent dielectric breakdown when point contacts were utilized.

No statistically significant difference in the properties was observed as a function of the

different facilities used in the measurements. Unfortunately, experiments planned for measurements of the properties of crystals under bias stresses were not conducted due to apparatus problems at NUWC.

Table 1: Results of protocol calculations for PZN-4.5%PT

Property	Alfred	NUWC	RMC	PSU	TRS
Sample Series	195	205 (3)	197	193	191
ε^T_{33} (s,MsE=0)	5515±349	4719±392	5572±388	5293±423	5239±280
d_{33} (<5 kV/cm) (pm/V)	1854 ± 31	1889 ± 56	1869 ± 61	1869 ± 89	1818 ± 13
ε^T_{33} (s,MIE = 0.635MV/m)		4041 ± 65	4203 ± 169	4095 ± 44	4141 ± 19
d_{33} (s,MIE =0.635MV/m), (pm/V)		1894 ± 91	1718 ± 84	1723 ± 19	1679 ± 74
ε^T_{33} (l,Ml)		3827±76	4288±145	4042 ± 76	3999±97
d_{33} (l,Ml), (pm/V)		1724±20	1684±84	1699±15	1658±69
Large signal tanδ		0.015 ± 0.003	0.031 ± 0.006	0.015 ± 0.003	0.013 ± 0.009
P_r (C/m^2) @ 1.5 MV/m		0.258 ±0.007	0.259 ± 0.001	0.240 ± 0.003	0.244 ± 0.002
E_c (MV/m) @ 1.5 MV/m		0.406 ± 0.038	0.373 ± 0.06	0.305 ±.003	0.320 ± 0.002

Table 2: Results of protocol calculations for PZN-8%PT

Property	Alfred	NUWC	RMC	PSU	TRS
Sample Series (#)	196	204 (1)	198 (4/2)	194 (5)	192 (3)
ε^T_{33} (s,MsE=0)	5442±600	4665±495	4965±1545	5038±682	5060±930
d_{33} (<5 kV/cm) (pm/V)	2878 ± 165		2753 ± 1132		2388 ± 165
ε^T_{33} (s,MIE = 0.635MV/m)		3789	3687 ± 495	3868 ± 461	3697 ± 286
d_{33} (s,MIE =0.635MV/m), (pm/V)		1574	2066 ± 277	1481 ± 483	1697 ± 81
ε^T_{33} (l,Ml)		3338	3552±495	3475±409	3482±229
d_{33} (l,Ml), (pm/V)		1890	1789±228	1690±272	1691±64
Large signal tanδ		0.051	0.071 ± 0.042	0.025 ± 0.018	0.038 ± 0.013
P_r (C/m^2) @ 1.5 MV/m		0.315	0.326 ± 0.002	0.388 ± 0.077	0.322 ± 0.004
E_c (MV/m) @ 1.5 MV/m		0.465	0.454 ± 0.008	0.316 ±0.015	0.463 ± 0.020

Table 3: Results of protocol calculations for PMN-26 ± 1%PT

Property	Alfred	NUWC	RMC	PSU	TRS
Sample Series (#)	213 (3)	223 (4)	215 (2)	209 (3)	211 (3)
ε^T_{33} (s,MsE=0)	4396±86	4463±142	4456±312	4489±44	4472±209
d_{33} (<5 kV/cm) (pm/V)	1189±41	1337±33	1220±72	1220±2	1199±24
ε^T_{33} (s,MlE = 0.635MV/m)	4271±235	3938±229	3758±34	3969±43	3768±132
d_{33} (s,MlE = 0.635MV/m), (pm/V)	1227±72	1420±97	1089±33	1100±56	1029±27
ε^T_{33} (l,Ml)	4009±134	4123±105	3793±16	3849±43	3859±181
d_{33} (l,Ml), (pm/V)	1424±211	1243±63	1075±26	1050±70	1304±497
Large signal tanδ	0.020 ±0.002	0.012 ±0.007	0.026 ±0.004	0.021 ±0.004	0.017 ±0.002
P_r (C/m^2) @ 1.5 MV/m	0.236 ± 0.002	0.243 ±0.011	0.244 ± 0.007	0.238 ± 0.001	0.235 ± 0.003
E_C (MV/m) @ 1.5 MV/m	0.198 ±0.024	0.280 ± 0.041	0.213 ± 0.018	0.218 ± 0.024	0.194 ±0.045

Table 4: Results of protocol calculations for PMN-29 ± 1%PT

Property	Alfred	NUWC	RMC	PSU	TRS
Sample Series (#)	214 (2)	224 (5)		210 (3)	212 (3)
ε^T_{33} (s,MsE=0)	5884±682	6100±266		6264±363	6498±269
d_{33} (<5 kV/cm) (pm/V)	1521±16	1669±181	samples	1784±8	1761±3
ε^T_{33} (s,MIE = 0.635MV/m)	5104±267	5022±405	not	5105±122	5090±151
d_{33} (s,MIE = 0.635MV/m), (pm/V)	1598±14	1629±214	provided	1570±37	1548±88
ε^T_{33} (l,MI)		4437±213		4826±49	4860±181
d_{33} (l,MI), (pm/V)		1331±81		1509±50	1461±84
Large signal tanδ	0.031 ±0.02	0.028 ± 0.006		0.028± 0.002	0.027± 0.008
P_r (C/m^2) @ 1.5 MV/m	0.243 ±0.006	0.243 ±0.011		0.184 ±0.081	0.247 ±0.004
E_C (MV/m) @ 1.5 MV/m	0.22 ±0.04	0.28 ±0.04		0.28 ±0.04	0.25 ±0.01

Figure 2: Unipolar Strain Field Data for PZN-4.5%PT

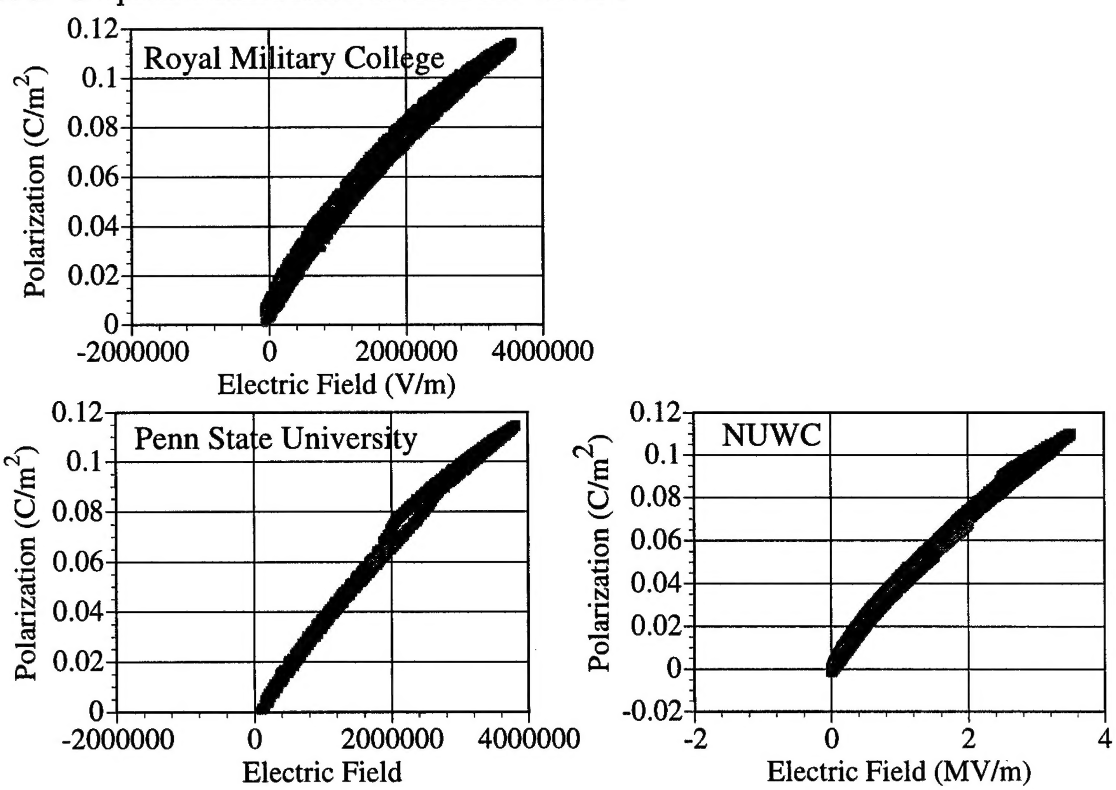


Table 5: NUWC calculations of the large signal properties for PZN-4.5%PT samples

Property	Alfred	NUWC	RMC	PSU	TRS
ε^T_{33} (l,Ml) @ 1.5 MV/m	--	4026 ± 126	4399 ± 197	4007 ± 61	4013 ± 153
ε^T_{33} (l,Ml) @ 2.0 MV/m	--	3765 ± 110	4089 ± 170	3770 ± 80	3661 ± 100
ε^T_{33} (l,Ml) @ 3.5 MV/m	--	3410 ± 134	3810 ± 308	3536 ± 63	3457 ± 200
d_{33} (l,Ml) @ 1.5 MV/m	--		1757 ± 149	1664 ± 33	1702 ± 27
d_{33} (l,Ml) @ 2.0 MV/m	--		1704 ± 115	1625 ± 29	1628 ± 44
d_{33} (l,Ml) @ 3.5 MV/m	--		1848 ± 234	1755 ± 116	1759 ± 144
Tanδ at 1.5 MV/m	--	0.030 ± 0.004	0.029 ± 0.019	0.027 ± 0.016	0.023 ± 0.006
Tanδ at 2.0 MV/m	--	0.025 ± 0.005	0.025 ± 0.012	0.019 ± 0.009	0.015 ± 0.001
Tanδ at 3.5 MV/m	--	0.039 ± 0.007	0.055 ± 0.008	0.043 ± 0.008	0.043 ± 0.003

Field induced rhombohedral to tetragonal phase transformations affect data

Table 6: NUWC calculations of large signal properties for PZN-8%PT crystals

Property	Alfred	NUWC	RMC	PSU	TRS
ε^T_{33} (l,Ml) @ 1.5 MV/m	--	3789	4268 ±814	4876 ± 1979	4750 ± 1594
ε^T_{33} (l,Ml) @ 2.0 MV/m	--	3789	5184 ±98	4576 ± 485	5045 ± 84
ε^T_{33} (l,Ml) @ 3.5 MV/m	--	4501	3642 ±149	3356 ± 25	3399 ± 93
d_{33} (l,Ml) @ 1.5 MV/m	--	1475	2234±502	2894 ± 1833	2701 ±1225
d_{33} (l,Ml) @ 2.0 MV/m	--	1528	3393±175	2381±781	3187±485
d_{33} (l,Ml) @ 3.5 MV/m	--	1735	2340 ± 80	2173 ± 63	2025 ± 126
Tanδ at 1.5 MV/m	--	0.074	0.090 ±0.031	0.251 ± 0.259	0.161 ± 0.112
Tanδ at 2.0 MV/m	--	0.062	0.179 ±0.085	0.456 ± 0.447	0.336 ± 0.040
Tanδ at 3.5 MV/m	--	0.106		0.155 ± 0.015	0.088 ± 0.048

Field Induced rhombohedral to tetragonal transformations

Table 7: NUWC calculations of the large signal properties for PMN-26 ± 1%PT samples

Property	Alfred	NUWC	RMC	PSU	TRS
ε^T_{33} (l,Ml) @ 1.5 MV/m	4625±227	4011 ±205	3620 ±164	3854 ± 65	3816 ± 11
ε^T_{33} (l,Ml) @ 2.0 MV/m	4211±170	3714 ±149	3397 ±155	3561 ± 77	3563 ± 80
ε^T_{33} (l,Ml) @ 3.5 MV/m	--	3173 ±60	3013 ±132	3131 ± 38	3132 ± 40
d_{33} (l,Ml)@1.5 MV/m	1255±264	1334 ± 67	1026 ± 52	978 ± 70	1060 ± 75
d_{33} (l,Ml)@2.0 MV/m	1309±169	1303 ± 52	998 ± 52	939 ± 82	1018 ± 87
d_{33} (l,Ml)@3.5 MV/m	--	1177 ± 47	954 ± 53	905 ± 49	980 ± 54
Tanδ at 1.5 MV/m	0.025 ±0.009	0.018 ±0.008	0.036 ±0.002	0.025 ± 0.010	0.024 ±0.011
Tanδ at 2.0 MV/m	0.029 ±0.011	0.015 ±0.006	0.033 ±0.002	0.024 ± 0.004	0.024 ± 0.004
Tanδ at 3.5 MV/m	--	0.015 ±0.007	0.029 ±0.002	0.022 ± 0.006	0.022 ± 0.005

Table 8: NUWC calculations of the large signal properties for PMN-29 ± 1%PT samples

Property	Alfred	NUWC	RMC	PSU	TRS
ε^T_{33} (l,Ml) @ 1.5 MV/m	--	4961 ± 265	samples	3546 ±414	
ε^T_{33} (l,Ml) @ 2.0 MV/m	--	4605 ± 332	not	3081 ± 240	
ε^T_{33} (l,Ml) @ 3.5 MV/m	--	3668 ± 194	provided		
d_{33} (l,Ml) @ 1.5 MV/m	--	1563±167		1593±153	
d_{33} (l,Ml) @ 2.0 MV/m	--	1549±217		1440±149	
d_{33} (l,Ml) @ 3.5 MV/m	--	1434±272			
Tanδ at 1.5 MV/m	--	0.042 ± 0.028		0.084 ±0.037	
Tanδ at 2.0 MV/m	--	0.059 ± 0.046		0.059 ±0.027	
Tanδ at 3.5 MV/m	--	0.034 ±0.021			